

Chapter I

Surfactant aggregation in solution

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1.1. General introduction

The "Surface Chemistry" is the branch of chemistry deals with the nature of the surfaces and also changes occurring on the surfaces of substances which may be liquid, gas or solid. The study of surface chemistry is not applicable for only academic interest but also for various technical applications of industry and our daily lives including different biological fields. In surface chemistry, we are concerned with the term "Surfactants" which comes from the common contraction of the term "Surface-active-agents". As the name suggest, they are the versatile chemical substances that modify the surfaces or interfaces of the systems in which they are contained. Surfactants have the ability to locate at the surfaces thereby altering significantly the physical properties of the interfaces [1, 2]. The interface at which a surfactant is adsorbed can be between two immiscible liquids, the liquid-gas (air) surface or between a solid and a liquid. This is due to the characteristics molecular structure of the surfactant molecules. Surfactant molecules have two parts in their molecular structure: a hydrophilic (polar) part which likes water or other polar molecules, and a hydrophobic (non-polar) part which does not like any other polar molecules but likes non-polar molecules. They are often also called amphiphiles. In short, the characteristic molecular structure of surfactants is amphiphilic in nature (from the Greek *amphi* meaning 'on both sides' and *philein* meaning 'to love') within the same molecular unit. The common schematic representation of the surfactant molecules is shown in **Figure 1.1**.

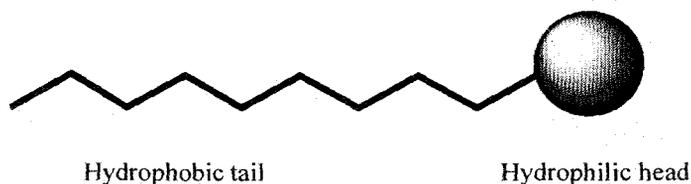


Figure 1.1 A common schematic representation of a surfactant molecule.

The non-polar part (water repelling or hydrophobic part) which generally consists of long chain hydrocarbon is also called a 'tail' whereas the polar part (water attracting or hydrophilic part) is termed as 'head'.

The hydrophobic part is of many different types, viz., aliphatic, aromatic or the mixture of both which generally originates from natural fats and oils, petroleum fractions, relatively short synthetic polymers, or relatively high molecular weight synthetic alcohols. The hydrophobic part is also less often halogenated or oxygenated hydrocarbon or sometime bears siloxane chain, where as the hydrophilic part is, in general, of four types, viz., cationic, anionic, nonionic and zwitterionic [2].

- (a) *Anionic*: In anionic surfactants, generally the carboxylates (soap), sulphates, sulfonates and phosphates are present with the hydrophobic part as hydrophiles which here acts as a surface active portion, e.g., RCOO-Na^+ (soap), $\text{RC}_6\text{H}_4\text{SO}_3\text{-Na}^+$ (alkyl benzene sulfonate). All of these still feature extensively in cleaning formulations.
- (b) *Cationic*: In cationic surfactants, generally some forms of amines are present with the hydrophobic part as hydrophiles which here act as a surface active portion, e.g., RNH_3^+ (salt of long chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Br}^-$ (quaternary ammonium bromide). The positive charge on the head group gives the surfactants a strong substantivity on negatively charged fibres, such as cotton, and they are, therefore, used in fabric.
- (c) *Non-ionic*: In non-ionic surfactants, the surface active portion bears no apparent ionic charges, e.g., $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride or long chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkyl phenol). They are used extensively in low-temperature detergency and as emulsifiers.
- (d) *Zwitterionic*: Zwitterionic surfactants often referred to as amphoteric surfactants. In this types of surfactants, there are both positive and negative part with the hydrophobic part as hydrophiles. These are often found in the form of $-\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ (betaines), $-\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{SO}_3^-$ (sulphobetaines) and $-\text{O-PO}_3\text{-CH}_2\text{CH}_2-\text{N}^+(\text{CH}_3)_3$ (lecithins/phosphatidyl cholines).

Apart from these four major types of surfactants, combinations of the above head group types are increasingly being used within a single surfactant. The most common are those that have both non-ionic and anionic groups such as the $-(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3^-$ (alkyl ethoxy sulphates). Surfactants of this type are mild on the skin and are, therefore, used in formulations where skin contact is not usually avoided.

In double chain surfactants, two hydrocarbon chains are attached to a polar head. On the other hand, Gemini surfactant contains two hydrophobic and two hydrophilic groups. Amphiphilic molecules can also have two head groups which may be both anionic, both cationic or one anionic and the other cationic, joined by hydrophobic spacer [2]. These types of molecules are termed "bola-amphiphiles" commonly known as "bolaforms" [3]. Surface activity of these molecules depends on both the hydrocarbon chain length and the nature of head group(s).

1.2. Aggregation of surfactant Molecules

Self-assembled surfactants or surfactant aggregates become popular to the researchers in recent years due to a huge benefit achieved in many industries producing detergents, cosmetics and pharmaceuticals which have surfactants as one of their constituents [4-6]. The spontaneous organization of molecules driven by intermolecular interactions into stable aggregates is the self-assembly of surfactants which is well recognized in biological systems, e.g., lipid bilayers, the DNA duplex, tertiary and quaternary structure of proteins. The process of spontaneous aggregation of simple molecules in solution into larger structures with a certain order is also an important phenomenon in every-day life as well as an interesting subject for scientific investigations. The best known example of aggregation in every-day life is the formation of "micelle" by surfactant or detergent molecules as has already been explained. The term micelle is used for an entity of colloidal dimension (radius of the colloid molecules $10^{-5} - 10^{-7}$ cm), in dynamic equilibrium with the monomer solution from which it is formed. The concentration at which the ions (head groups) are pulled into the bulk of the solution and form a cluster of molecules in which hydrophobic tails are in the interior of the cluster and ionic ends are at the surface of the cluster is

known as critical micelle concentration (cmc). Above the critical micelle concentration of the surfactant concentration, the addition of fresh monomer results in the formation of new micelles. Here the monomer concentration remains essentially constant and equal to the cmc. Due to three dimensional hydrogen bonding of water molecules, it has an open structure which permits the existence of clusters of water molecules containing cavities with specific sizes which can accommodate non-polar chains [7-9]. Creation of the cavity restricts the motions of solvent molecules in the hydration shell of a non-polar solute. This restriction leads to loss of entropy, which is exceptionally large in aqueous solution due to the small size of water molecules [8-12]. For a given surfactant, at a given temperature, only a certain amount of monomer can be accommodated in the cavities and any further addition of surfactant will result in the formation of micelles. In other words, the further addition of surfactant provides a driving force to minimize contact of the monomer hydrocarbon chains with water. Therefore, according to Langmuir's principle of differential solubility, the hydrocarbon chains cluster to form a core (micellar core) while the polar groups interact with the water [13]. Each micelle consists of a certain number of monomer molecules (aggregation number, n) which determines its general size and shape. The exact size and shape of micelles is still uncertain but that of an ionic micelle in dilute salt-free conditions it is known to be spherical [10]. The region adjacent to the stern layer contains a high density of counter ions of the polar heads (Gouy Chapman double layer) and separates the hydrophobic interior from the bulk aqueous phase [14].

1.3. Structure and shape of micelles: The molecular packing parameters

In solution, a dynamic equilibrium exists between surfactant monomers and micelles. Therefore, it may be to some extent unrealistic considering them to be rigid with precise structures and shapes. The spherical shape of the micelle was conceived by Hartley [15]. The micelle having regular shape are supported by different studies of micellar solutions, viz., dynamic light scattering (DLS) studies, Small-angle neutron scattering (SANS) studies, phase diagram studies etc [16-24]. The general assumption is that the micelles at critical micelle concentration are roughly spherical. The radius of a micelle cannot be greater than the stretched-out length of the surfactant molecule. Typically micelles may have average radii of 1.2 - 3 nm and can contain 5 - 100

monomer units. Other proposed structures of micelles are rod-like [25], lamellar model [26], cylindrical model [27] etc. Added electrolyte has great influence on the shape of ionic micelles. As the counterion concentration is increased, the shape of ionic micelles changes in the sequence spherical - cylindrical - hexagonal - lamellar [17-18, 21, 28-30]

The molecular packing parameter allows a simple and also intuitive insight into the self-assembly phenomena and that is why it is most cited in different science subjects and topics [31-32]. The packing parameter approach permits indeed to relate the shape of the surfactant monomer to the aggregate morphology [33-35]. The molecular packing parameter P is defined as the ratio $v/a_0 l_c$, where v and l_c are the volume and the extended length of the surfactant tail, respectively and a_0 is the equilibrium area per molecule at the aggregate interface (or mean cross-sectional (effective) head-group surface area), as illustrated in figure 1.2. If we consider a spherical micelle with a core radius R , made up of N_{agg} molecules, then the volume of the core is $V = N_{agg} \times v = 4 \pi R^3/3$, the surface area of the core $A = N_{agg} \times a_0 = 4\pi R^2$. Hence, it can be deduced that $R = 3 v/a_0$, from simple geometric relations. If the micelle core is packed with surfactants tails without any empty space, then the radius R cannot exceed the extended length l_c of the tail. Introducing this constraint in the expression for R , one obtains $0 \leq v / a_0 l_c \leq 1/3$, for spherical micelles. These geometrical relations, together with the constraint that at least one dimension of the aggregate (the radius of the sphere or the cylinder, or the half-bilayer thickness, all denoted by R) cannot exceed l_c , lead to the following well-known connection between the molecular packing parameter and the aggregate shape [33], i.e., $0 \leq v/a_0 l_c \leq 1$ for bilayers. Inverted structures are formed when $P > 1$. This can be easily understood from a figure showing the critical packing parameter with head group area, extended length and the volume of the hydrophobic part of a surfactant molecule. From this figure, it can also be concluded that the radius of a micelle cannot be greater than the stretched-out length of the surfactant molecule.

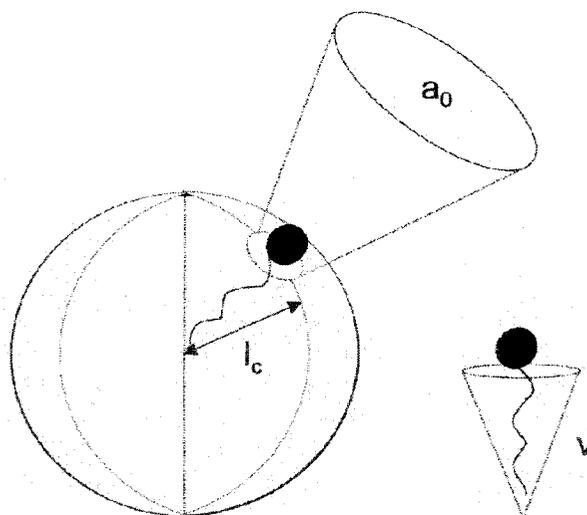
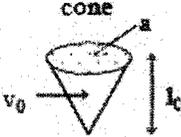
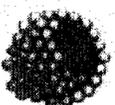
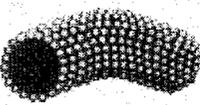
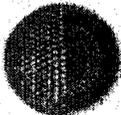
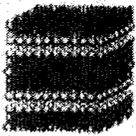
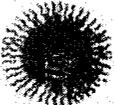


Figure 1.2. The critical packing parameter P (or surfactant number) relates the head group area, the extended length and the volume of the hydrophobic part of a surfactant molecule into a dimensionless number $P = v / a_0 l_c$.

Therefore, if the molecular packing parameter is known, the shape and size of the equilibrium aggregate can be readily identified. Nagarajan showed that the tail length influences the head group area (considering the tail packing constraints) and thereby the micellar shape [32]. It is important to note that a_0 is often referred to as the “headgroup area” in the literature. This has led to the erroneous identification of a_0 as a simple geometrical area based on the chemical structure of the headgroup, although a_0 is actually an equilibrium parameter derived from thermodynamic considerations [32]. Needless to say, that for the same surfactant molecule, the area a_0 can assume widely different values depending on the solution conditions such as temperature, salt concentration, additives present, etc.; hence, it is meaningless to associate one specific area with a given head group. For example, sodium dodecyl benzene sulfonate forms micelle in aqueous solution whereas bilayers structures are formed when alkali metal chlorides are added [35] resulting different a_0 values in these two cases. Moreover, the role of the surfactant tail has been virtually neglected. This is in part because the ratio v / l_c appearing in the molecular packing parameter is independent of the chain length for common surfactants (0.21 nm^2 for single tail surfactants) and the area a_0 depends only on the head group interaction parameter. The predicted aggregation characteristics of surfactants are presented in Table 1.1.

Table 1.1. Schematic representation of surfactant structures and shapes derived from various packing parameters.

Possible surfactant type	$P (= v / a_0 l_c)$	Shape	Structure formed
Single-tail surfactants with large head groups	$< 1/3$	cone 	spherical micelles 
Single-chain surfactants with small head groups	$1/3 < P < 1/2$	truncated cone 	cylindrical micelles 
Double-chain surfactants with large head groups and flexible chains	$1/2 < P < 1$	truncated cone 	flexible bilayers, vesicles 
Double-chain surfactants with small head groups or rigid, immobile chains	$P \sim 1$	cylinder 	planar bilayers 
Double-chain surfactants with small head groups, and bulky chains	$P > 1$	inverted truncated cone or wedge 	inverted micelles 

1.4. Amphiphiles in aqueous medium

The most intensely studied and debated type of molecular self-assembly and perhaps the simplest in terms of the structure of the aggregate is the micelle. They are loose, mostly spherical aggregates above their critical micellization concentration (cmc) in water or organic solvents. The schematic representation of a spherical micelle in aqueous solution is shown in Figure 1.3. In this figure, the hydrophobic chains are directed towards the interior of the aggregates and the polar head-groups points towards water, hence allowing the stability/solubility of the aggregate (no phase separation) [2].

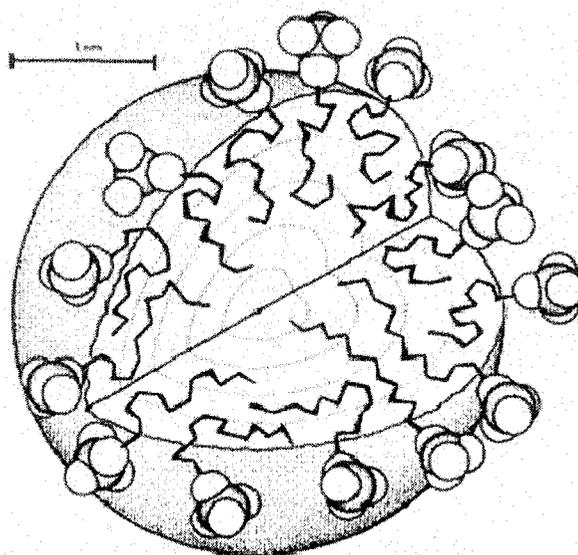


Figure 1.3. Schematic representation of a spherical micelle in aqueous solution.

As stated earlier, micelles are in dynamic equilibrium with the monomer from which it is formed. The physical properties of the surfactants are different in pre-micellar and post micellar region. It is interesting to note that although it is usually assumed that there are fairly well-defined water layers around the micelle surface, there is no agreement on the composition of the micellar core [36], i.e., whether it consists of pure hydrocarbon or of hydrocarbon mixed with water is not certain. The penetration of water molecules in the micellar core [37] is still a matter of controversy.

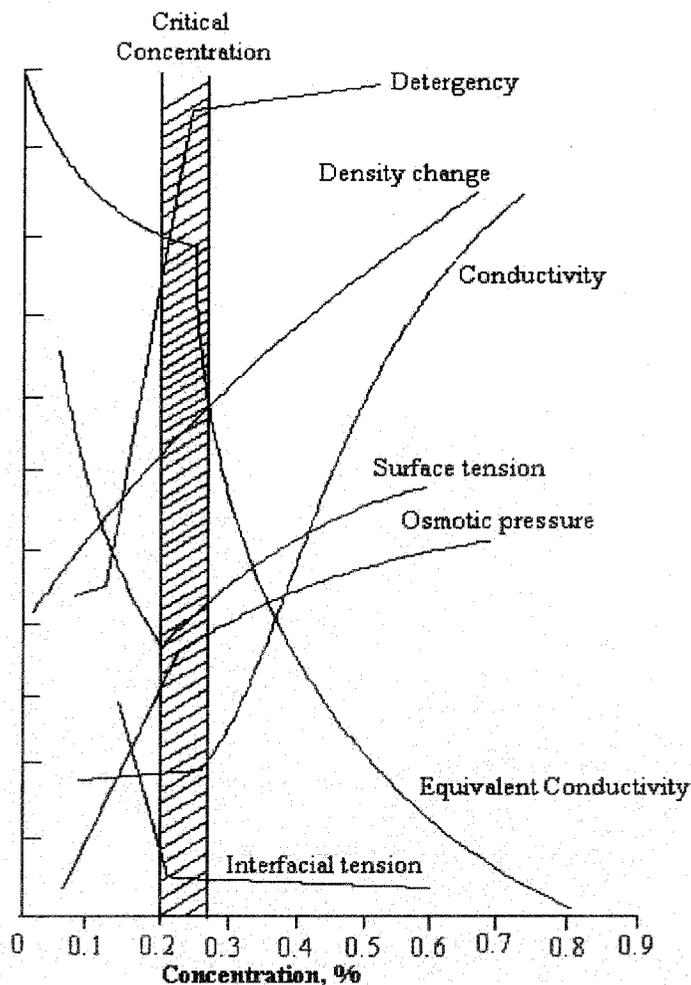


Figure 1.4. Schematic representation of the concentration dependency of some physical properties for solutions of a micelle forming surfactant.

All types of surfactants viz., cationic, anionic, nonionic and also zwitterionic, can form micelles in aqueous solutions. An important criterion of a versatile solvent is to form hydrogen bonds as like water molecules. When the non-polar unit of the surfactants is introduced in water, the hydrogen bonding network of water molecules is (Figure 1.5) disrupted and the water molecules order themselves around the nonpolar part to satisfy hydrogen bonds resulting in an unfavourable decrease in entropy in the bulk water phase.

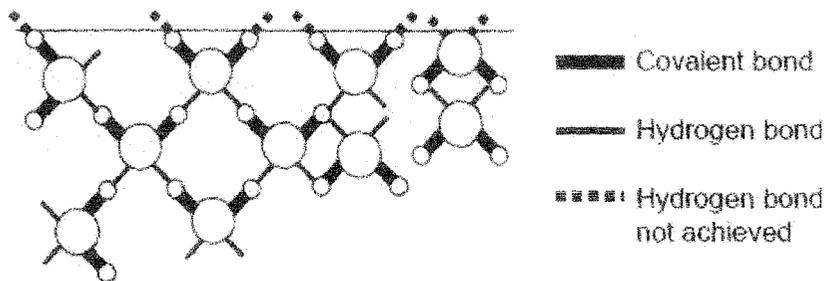


Figure 1.5. Water molecules at the liquid-air interface.

As additional non-polar units are added to the solution, they self-associate and reduce the total water-accessible surface of the complex relative to the monodisperse state. Now, fewer water molecules are required to rearrange around the collection of non-polar groups (Figure 1.6). As a result, entropy associated with the complex is less unfavourable than for the monodisperse detergents. In short, hydrophobic association and the formation of micelles is driven by the favourable thermodynamic effect on the bulk phase of water.

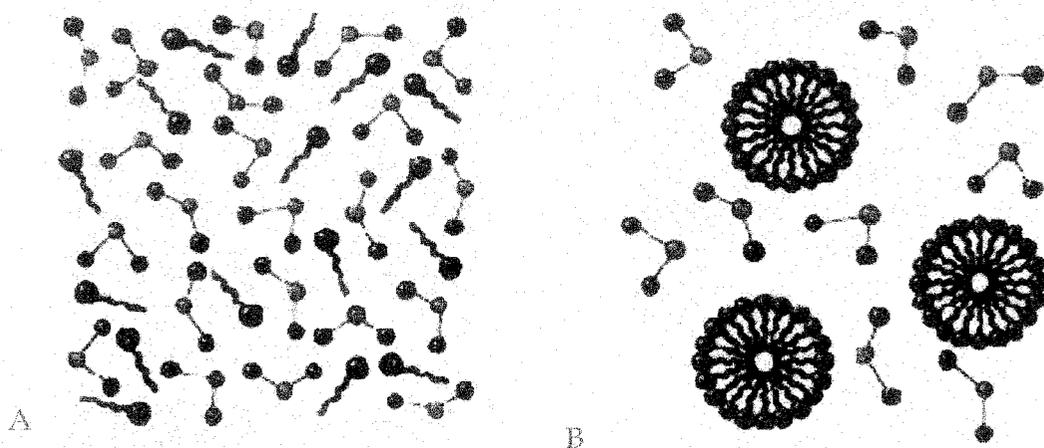


Figure 1.6. (A) Water molecules ordered around surfactant monomers. (B) Loss of total water-accessible surface as a result of micellization.

Only average shape and aggregation number of a micelle can be determined due to its short life-span in dynamic equilibrium. Micellization is the results of the hydrophobic effect present in the surfactant molecules. In micellization there are two opposing forces working together. The first is the hydrophobicity of the hydrocarbon tail, favoring the formation of micelles and second is the repulsion between the surfactant head groups. The mere fact that micelles are formed from the ionic surfactants is an indication that the hydrophobic driving force is large enough to overcome the electrostatic repulsion arising from the surfactant head groups. A large

number of theoretical and experimental researches by different methods have been carried out to understand the structure and thermodynamic and other property of the micelles employing various methods [38-40].

The controversial "water exposure of micelles" concept [41, 42] discusses in terms of predictions of the main characteristics of the molecular conformation of micelles by using "phase separation model" or "mass action model" [43-45]. These models predictions are in agreement with the experimental data with the following assumption with some principal features of micellar structure.

- (I) The micellar core is virtually devoid of water, according to Langmuir's original principle of differential solubility.
- (II) Micellar chains are randomly distributed and steric forces determine the final structure.
- (III) Contact of the hydrophobic sections of the micelle with water results from a disordered structure in which the terminal groups or chain ends are near the micellar surface and thus exposed to bulk water [46].

The mass action model along with the related thermodynamics of micelle formation is discussed in chapter III.

A lot of research work has been devoted by numerous workers to elucidate various factors responsible for cmc [47]. Among the factors that are known to affect the cmc in aqueous solutions are:

- (I) The structure of the surfactant
- (II) The presence of added electrolyte (in the case of ionic surfactants) in solution
- (III) The presence of various organic compounds in solution, and
- (IV) Temperature of the solution.

Surfactant structure: Generally it is known that the non-ionic surfactants have lower cmc values as compared to the ionic surfactants and this cmc value decreases with the increase in hydrophobicity of the surfactant molecules. It is also known that the cmc value becomes halved by addition of one methylene group to the hydrocarbon tail. But this decrease is not similar incase of nonionic and zwitterionic surfactants. It is known

that the cmc decreases in case of nonionic and zwitterionic surfactants to one fifth of its previous value on addition of one methylene group to the hydrocarbon tail. The unsaturation of hydrocarbon chain has also great influence on the cmc value. It is also known that the increase of unsaturation increases the cmc of the surfactant. On the other hand, introduction of a polar group such as - O or - OH to the hydrocarbon chain increases the cmc to a significant extent. However, replacement of hydrocarbon chain by a fluorocarbon chain of same length causes a decrease in cmc values. For n-alkyl ionic surfactants, the cmc decreases in the order ammonium salts > carboxylates > sulfonates > sulfates. It has also been found that in quaternary cationics, trimethylammonium compounds have higher cmc's than the corresponding pyridinium compounds.

Counterion: With changes of the counterion, the cmc value of the surfactant changes significantly. The degree of counterion binding plays an important role in determining the value of cmc. For alkali metal counterion and also for other counterions, with increase in the hydrated radius, cmc increases. This cmc increase is due to the weaker counterion binding with increase in hydrated radius of the counterions. In aqueous solution, the cmc values of sodium dodecyl sulfate with different counterion shows the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{NH}_4^+ > \text{N}(\text{CH}_3)_4^+ > \text{N}(\text{C}_2\text{H}_5)_4^+$. Also similar variation is seen for the cationic surfactants with change in anionic counterions. For cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order of cmc in aqueous solution are $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

Electrolytes: With addition of electrolytes to a surfactant solution, the cmc value decreases to a certain extent. But this decrease is very small for nonionic surfactant as compared to the cationic and anionic surfactants. Also for zwitterionic surfactant this decrease is much higher as compared to the anionic or cationic surfactants due to the stronger interactions of the surfactants and electrolyte present in the solution. Screening of charge by the ions of the added electrolyte to the head group of surfactant is mainly responsible for the decrease in cmc values. Added electrolyte has great influence on the shape and aggregation number of the ionic micelles. As the counterion concentration is increased, the shape of ionic micelles changes in the

sequence spherical – cylindrical – hexagonal – lamellar. The different forms of micelle are shown in figure 1.7.

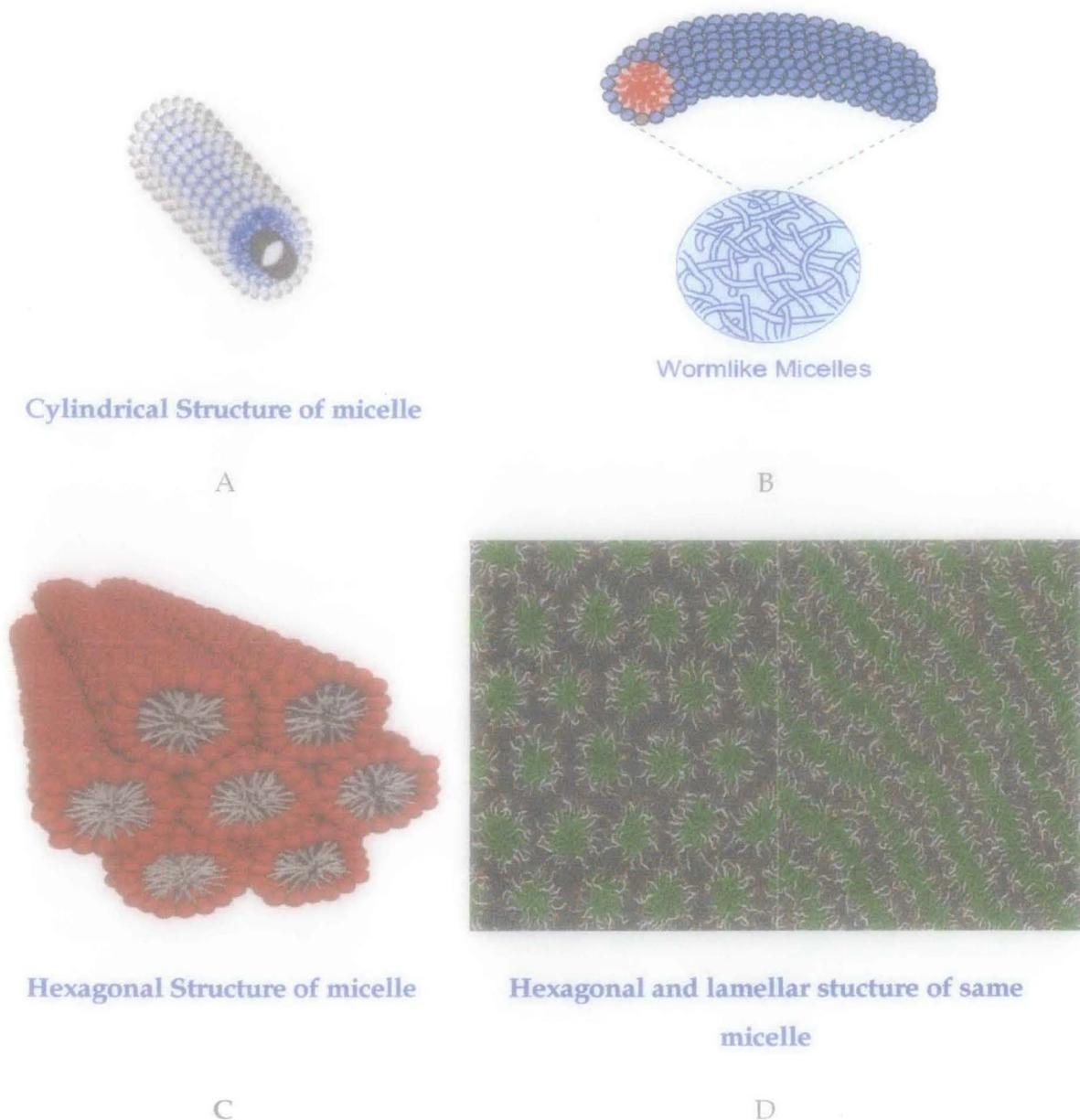


Figure 1.7. (A) Structure of a cylindrical micelle. (B) Microstructure of a typical wormlike micelle formed from cylindrical micelle. (C) Hexagonal shape micelle (D) Structural changes from hexagonal micelle to lamellar micelle.

But the charge screening effect is not responsible for nonionic and zwitterionic surfactants. Here, mainly “salting out” and “salting in” of the hydrophobic group in aqueous solvents are responsible for decrease in cmc.

Organic additives: Polar organic compounds such as alcohols with longer chains and water miscible properties generally decrease the cmc of surfactants to a much lower concentration than in aqueous solutions. But shorter chain length alcohols with high degree of polarity, the effect will be reverse. So, the effect of alcohols on the cmc of the surfactants depends on the chain length and the solubility of the alcohol present in the systems. Alcohols with short chain length are mainly adsorbed in the water-micelle interfacial region but alcohols with longer chain length are adsorbed in the outer portion of the micellar core. On the other hand, additives like urea, formamide, guanidinium salts, fructose and xylose increases the cmc to relatively higher concentrations by modifying the interaction of surfactant molecules with water. When the surfactants aggregate in non polar solvents, their polar or charged groups are located in the interior, or core, of the aggregate, while their hydrocarbon tails extend into the bulk solvent. These aggregates are referred to as reverse micelles (Figure 1.8).

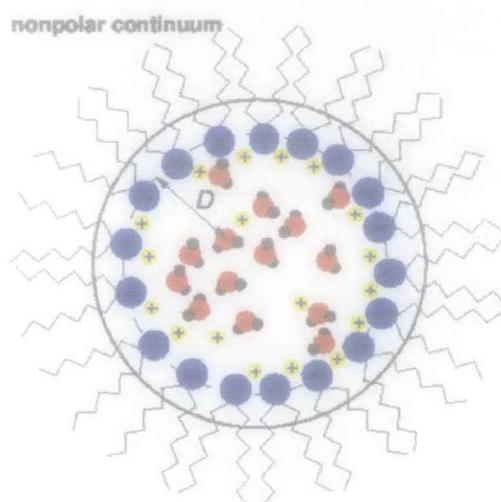


Figure 1.8. Schematic representation of a reverse micelle formed from a double tailed surfactant.

Temperature: The effect of temperature on the cmc of surfactants in aqueous solution is generally first to decrease with temperature and then to increase with temperature passing through a minimum in between these two. But there are also other types of variation observed in the literature, for example, with increase in temperature the cmc of the surfactant increases. Increase of temperature causes decrease of hydration of the hydrophilic group, which favours micellization and also causes disruption of the structured water surrounding the hydrophobic group. This disfavors micellization.

The relative magnitude of these two opposing effects, therefore, determines increase or decrease of the cmc value. Pronounced effect of temperature appeared in case of double chain surfactants. It is known that turbid, liposomal dispersions of didecyldimethyl ammonium bromide at room temperature become a clear solution when heated to 60°C due to formation of small micellar aggregates [48-49].

1.5 Aggregation number of micelle

An aggregation number of a micelle is defined as the number of surfactant molecules present in a micelle once the critical micelle concentration (cmc) has been reached. It is one of the most important and fundamental structural parameters of micellar aggregates [50]. Different methods are employed to determine the aggregation number of the micelles. The value of the aggregation number contains information on the micellar size and shape, which may be important in determining stability and practical applications of the investigated systems [50-52]. Generally, aggregation number of a micelle can vary from 10 to 100. But in the literature, aggregation number of 3 is also reported. Further, the aggregation number changes with the solvent or electrolyte present in the systems. It has been observed by different researchers that the addition of electrolyte generally increases the aggregation number of the micelles. Among the different methods employed to determine the aggregation number, fluorescence probe method is one of the important techniques. In this method, a quencher is added from the outside to the system. And fluorescence intensity is measured with the change of quencher concentration. From these data, aggregation number can be calculated. This method is very popular due to easy availability and handling of the instruments (Fluorescence Spectrophotometer) and also simplicity of the technique. It has been found that the bile salts, which are the main products of cholesterol metabolism, has the aggregation number of 3 (three), as measured by different methods [53]. Similarly, the study of sodium dodecyl micelles in presence of aluminium salt shows the average number of 250 which is much higher than the aggregation number of the same surfactant in aqueous solution [54]. Large volume of the research has been carried out for anionic micelles with sodium dodecyl sulfate [55-58]. It is also known that surfactants with smaller aggregation numbers tend to form more spherical micelle while surfactants with larger aggregation

numbers tend to form ellipsoid micelles. In general, aggregation numbers increase as the length of the hydrocarbon chain increases. Aggregation numbers tend to decrease as the size of the hydrophilic group increases and upon the addition of hydrocarbons and polar compounds to surfactant solutions [59]. Increasing the temperature of solutions of ionic surfactants also causes an increase in the aggregation number. In short, the factors that increase the aggregation numbers are (i) increasing number of methylene groups in the alkyl chain (ii) addition of counterions (for ionic surfactants) whereas the factors that responsible for decrease in aggregation number of a surfactants are (i) increasing size of hydrophilic head group (ii) polar organic additives (iii) Addition of hydrocarbons to solution.

1.6. Oxazine Dye

Photo-induced electron transfer processes in surfactant solutions are potentially important for efficient energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface [60-63]. The visible absorption spectra of organic dyes exhibit a strong dependence on concentration in aqueous solution because of aggregation [64-65]. Aggregation affects colour, solubility and photophysical behaviour of dyes. Self association of fluorescent dyes often leads to self quenching. It plays key roles in many technological applications such as opto-electronic devices, optical logical elements etc. Important examples include sensitization of silver halide nanocrystals in photographic processes and nonlinear optical materials [66-71]. A systematic study of the aggregation characteristics of dyes from spectrophotometric data has become a useful field of research because of its possible application in understanding such phenomena on energy transfer in biological systems, metachromatia, hypochromism, conformation of polypeptides, and staining properties of dyes for biological specimens. The force responsible for holding the component molecules in the dimer or in polymer is not yet well understood. Nevertheless, it is clear that for ionic dyes, aggregation would be possible if there exists some very strong attractive interaction, which first of all overcomes the coulombic repulsion and then brings the component molecules to a reasonable distance to form dimers and subsequently high polymers. Photochemical

systems for photoreduction of water and photoinduced electron transfer reaction in surfactant solutions are of considerable interest as models for understanding of photobiology [72-73] and the conversion of solar energy [74-75]. Compared to inorganic complexes, organic dyes have been investigated only rarely as sensitizers for the photo-reduction of water [74-76].

The properties of oxazine dye aggregates at liquid/solid interfaces have been of interest for long time. It was suggested that solar energy harvesting with wide band gap semiconducting photoconductors may be improved by covering with this dyes to expand the wave length range [68]. The oxazine dyes display surprisingly long wave length absorption and emission maxima given their small sizes and as such have been shown to be important fluorescent probe for biological systems [69-70]. They can be excited with simple laser sources such as solid state laser diodes. Oxazine dyes are also finding increasing applications in the field of electrocatalysis of electrochemical redox processes. Oxazine dye modified electrodes have been shown to be useful in electrocatalytic oxidation of coenzyme NADH in the context of enzyme based biosensors [71]. Examples of oxazine dyes are: oxazine 1, oxazine 170, cresyl fast violet etc. These types of dye have similar structure as that of methylene blue which is one of the most investigated substance in the relevant field of research. The structure of cresyl fast violet is given in figure 1.9:

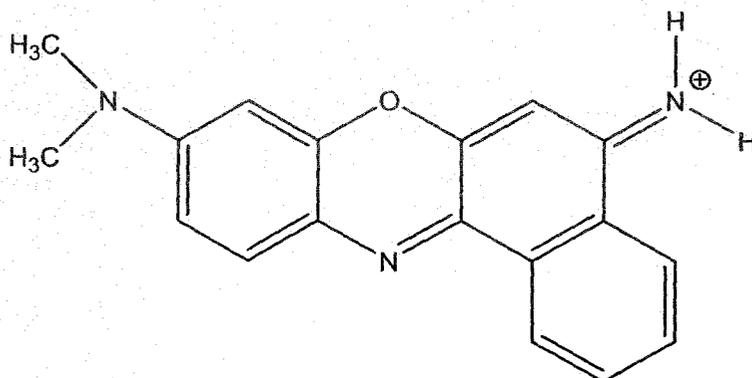


Figure 1.9.: Schematic representation of Cresyl fast violet.



Oxazine dyes are known to form non-fluorescent H-aggregates, which have the dimers stacked on top of each other (π -stacked dimers). In H aggregates, only transitions to the higher of the two states are allowed which means that the light

absorbed by these dimers to make this transition will be of higher energy, and therefore blue-shifted from the light absorbed by the monomer.

1.7. Dye-Surfactant Interactions in Aqueous Medium

Surfactants exert profound effects on many chemical reactions and interactions arise mainly from change in the local environments and concentrations of interacting species due to the interactions with the surfactant micelles. In order to elucidate the nature of effects of surfactants and to design desirable surfactant systems, it is essential to understand the nature of interactions between probe molecules and surfactants [77]. The dye-surfactant systems have attracted considerable amounts of interest in recent years. The enhanced energy transfer between dyes in dye-surfactant systems made them good model membrane systems of chloroplast [78-81]. The peculiar behavior in both absorption and fluorescence spectra of dyes in the presence of surfactants of opposite charge were attributed to the formation of a continuum of dye - surfactant aggregates: dye ratio (S/D) [82-86]. Photoinduced electron transfer processes in surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface. Dye surfactant interactions are generally complex [87]. In dye surfactant interactions, molecular complexes having specific and characteristics physicochemical features may be formed. Also, physico-chemical properties of the adsorbed dye can be controlled with ease by the incorporation of some oppositely charged surfactant assembly. The very high polarity (large dielectric constant) of water arises principally from the extended hydrogen bond network and mutual polarization of the water molecules in close proximity. Because of polarization, the dipole moment of water in the liquid phase (2.6 D) is higher than that in vapour (1.85 D). A water molecule bound to a dye molecule cannot polarize another water molecule. This causes a marked reduction in the dielectric constant of the hydration layer of an organized assembly compared to bulk water and hence the dye-surfactant interactions in aqueous solution is also important to know the interaction thoroughly. From early times, the colour changes of ionic dyes in presence of surfactants in aqueous solution have led many researchers to propose dimer and multimer formation of dye molecules in the surfactant micelle, this area is still important and interesting for theoretical, ecological and technological point of view [88-89]. The interest in fluorescent dyes for qualitative and quantitative assays

has increased considerably during the last few decades. The sensitivity, simplicity and selectivity of fluorescent-based techniques make them particularly attractive for *in vitro* and *in-vivo* cellular and molecular biology studies. There are several major advantages of using fluorescent dyes that absorb in the red over those that absorb at shorter blue and green wavelengths. The most important of these advantages is the reduction in background that ultimately improves the sensitivity achievable. There are three major sources of background: (I) elastic scattering, i.e., Rayleigh scattering, (ii) inelastic scattering, i.e., Raman scattering and (III) fluorescence from impurities. The efficiencies of both Rayleigh and Raman Scattering are dramatically reduced by shifting to longer wavelength excitation. Likewise, the number of fluorescent impurities is significantly reduced with longer excitation and detection wavelength. Besides reduced background, a further advantage is that of low-cost and energy efficient system. A recent report demonstrates that the use of red-absorbing fluorescent labels and diode laser excitation at 635 nm provides sufficiently low autofluorescence of biological samples so that individual antigen and antibody molecules can be detected in human serum samples [90-95]. Among other things, the investigations into the behaviour of different dyes in surfactant aqueous solutions, give useful information about the mechanisms according to which surfactants operate as leveling agents and provide information on the influence of dye-surfactant interactions on the thermodynamics and kinetics of dyeing process. This may directly affect the quality of dyeing, which is one of the goals of textile finishing. To understand the chemical equilibrium, mechanism and kinetics of surfactant sensitized colour reactions, the knowledge of dye-surfactant interaction should also be a great value. Surfactants are also used as solubilizers for dyes which are insoluble in water, to break down aggregates of the dye in order to accelerate adsorption process on fiber, as auxiliaries for improving dye adsorption and as leveling or dispersing agents [96-98]. According to the structures of dye and substrate, surfactants used as leveling agents operate by different mechanisms. It seems probable that once the electrostatic forces have brought together the oppositely charged molecules, hydrophobic interactions take place, dramatically changing the microenvironment experienced by the chromophore. Therefore, a great deal of research work focused on dye-surfactant interactions in binary mixtures including the interactions between ionic dyes and ionic surfactants of the opposite and the same charges, ionic dyes and nonionic surfactants

as well as between nonionic dyes and ionic or nonionic surfactants in the submicellar and micellar concentration ranges of surfactants have been performed [98-104].

It has been observed by Carroll et. al. that sodium dodecyl sulfate in presence of different oxazine dye displays evidences of intermolecular interactions via spectrofluorometric method. The absorption spectra and the emission spectra change with the concentration of the surfactant in different ways. Also with the change of dye, the premicellar and postmicellar spectrophotometric characteristics changes showing different types of interactions with different dyes.

1.8. Effect of addition of a surfactant to the aggregation of another surfactant.

Above the critical micelle concentration (cmc), hydrophilic surfactants form small globular micellar aggregates and the solutions show Newtonian flow behaviour. Compared to single surfactant, the mixed surfactant exhibits superior interfacial properties such as higher surface activity and lower critical micelle concentration (cmc). Various such surfactant mixtures have been studied including cationic/anionic, non ionic/non ionic, cationic/non ionic, anionic/non ionic, cationic/cationic surfactants etc. Surfactant mixtures are commonly preferred in medicinal and pharmaceutical formulations and industrial preparations due to the purpose of suspension, solubilization and dispersion. Ionic surfactants can also self assembled to long thread-like or worm-like micelles in presence of certain organic ions e.g., sodium salicylate. Under certain conditions such as concentration, salinity, temperature, presence of counterions, etc., the globular micelles may undergo uniaxial growth and form very long and highly flexible aggregates, referred to as "wormlike" or "threadlike" micelles [105 - 112]. Wormlike micelles [106] are long, self-assembled, semi-flexible, breakable polymers with surfactant heads on the outside and tails in the core and display a striking range of dynamical properties, including anomalous relaxation, shear banding, and rheological chaos [113-114]. Due to this reason, wormlike micelles have received considerable attention from theoretician and experimentalist during the past few decades. A dramatic influence on the viscosity of wormlike micelles in aqueous solutions of CTAB was shown for *trans-ortho*-methoxycinnamic acid [115]. Through this development it became clear that by mixing surfactants (hydrotropes) of opposite charges, cationic and anionic, but with varying chain lengths, one can control the degree of precipitation of the surfactants to produce

different supramolecular structures like vesicles and polymeric micelles [116]. The transition from one structure to another is also well known facts in recent studies. A temperature-induced vesicle to micelle transition has been claimed for a system of cationic surfactant e.g., cetyltrimethylammonium 3-hydroxy naphthalene 2-carboxylate [117].

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